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BIOACTIVITY OF CONTROLLED RELEASE FORMULATIONS OF STARCH-ENCAPSULATED EPTC*

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Using a bioassay technique, the biological activities of starch-encapsulated formulations of EPTC (S-ethyl dipropylthiocarbamate) were determined in relationship to their controlled release characteristics. The bioactivity of the highly volatile herbicide EPTC was retained on a wet soil surface for 6 to 8 days by starch encapsulation utilizing several crosslinking processes (both chemical and non-chemical) and starches with different ratios of amylopectin to amylose. The rate of release, a measure of the integrity of the granule, depended on the nature of the starch and the crosslinking process. With the herbicide EPTC, encapsulation with a pearl or high amylose starch utilizing the jet-cooking process produced the best controlled release formulation even under the most adverse conditions.

INTRODUCTION

The technology for the encapsulation of pesticides within a starch matrix has progressed rapidly over the last decade. The first modified starch process involved xanthates (SX), resulting in matrices exhibiting controlled release characteristics [1,2]. The rate of release was found directly related to the oxidants used in crosslinking reactions [3–5]. Because of the toxic carbon disulfide used in the xanthate process, further developments were pursued, resulting in a calcium (Ca) [6], a borate (B) [7], and a calcium–borate (Ca–B) procedure [8]. All of these new technologies were used to prepare effective controlled release formulations of relatively high volatile herbicides [4,5,8]. It is important to note that all of the above procedures chemically modified the starch.

More recently, encapsulation has been accomplished without solubilizing the starch with chemicals, i.e., utilizing steam-jet cooking (JC) and crosslinking by the natural process of retrogradation [9]. Using butylate (*S*-ethyl diisobutylthiocarbamate), a highly volatile herbicide (VP 13×10^{-3} mm at 25°C), the authors were able to show efficiency of encapsulation. In addition, the rate of release varied with temperature and starch concentration during cooking, amount of herbicide incorporated, and

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method of drying. They also were able to show that the rate of release was directly related to the amylose content of the starch used [10].

Although the physical and chemical characteristics indicate controlled release, the final test is to determine the biological activity over time.

MATERIALS AND METHODS

a. Formulations

All of the formulations used in this study were prepared at the Northern Regional Research Center, Peoria, IL using an emulsifiable concentrate (7E) formulation of EPTC (*S*-ethyl dipropylthiocarbamate) to make up all starch samples.

b. Starches

Corn starches from CPC International (pearl, Globe 3005), American Maize-Products (waxy, Amioca), and National Starch and Chemical Co. (high amylose, Amylon VII) were used for all encapsulations as listed in Table 1.

c. Bioassays

Three replicated series of bioassays were conducted using the formulations listed in Table 1. EPTC was selected as the bioactive agent because of its high volatility (VP 34×10^{-3} mm at 25 °C) and loss by vaporization when applied to the surface of wet soils without incorporation. When applied to dry soil it is adsorbed to clay and organic matter but can be readily released by wetting.

The various formulations (all 20–40 mesh size) were surface applied uniformly at 3.36 kg/ha to 9 cm^2 plastic petri dishes containing 135 g of silt loam soil wetted to field capacity. The soils were kept at field capacity by a filter paper wick which was placed under the soil of each dish at time of filling and inserted into a well of water for specified periods of time. In each series of bioassays an untreated check and an emulsifiable concentrate (EC) were used for comparison (Fig. 1). After specified periods of time left uncovered and with exposure to the atmosphere, they were bioassayed using pregerminated oat seeds according to the method of Horowitz [11]. Shoot growth was measured 48 hours after bioassays were initiated.

Series 1 was a comparison of the waxy Ca-B, waxy JC, EC and untreated check exposed on a

TABLE 1

Characteristics of EPTC formulations based on initial starch type used and method of crosslinking

Starch type	Crosslinking chemical	Ref.	% EPTC active ingredient	Product pH	Swelling (%)
Pearl	borate	7	6.5	9.74	760
Pearl	calcium-borate	8	5.8	9.33	680
Pearl	calcium	6	7.2	11.54	800
Waxy	calcium-borate	8	5.1	9.43	840
High amylose	calcium-borate	8	2.3	9.38	220
Pearl	$FeCl_3$-Xan	1	6.4	2.80	200
Waxy	none[a]	9	6.5	5.68	840
Pearl	none[a]	9	4.4	6.37	220
High amylose	none[a]	9	5.2	5.82	180

[a]Retrogradation after jet-cooking.

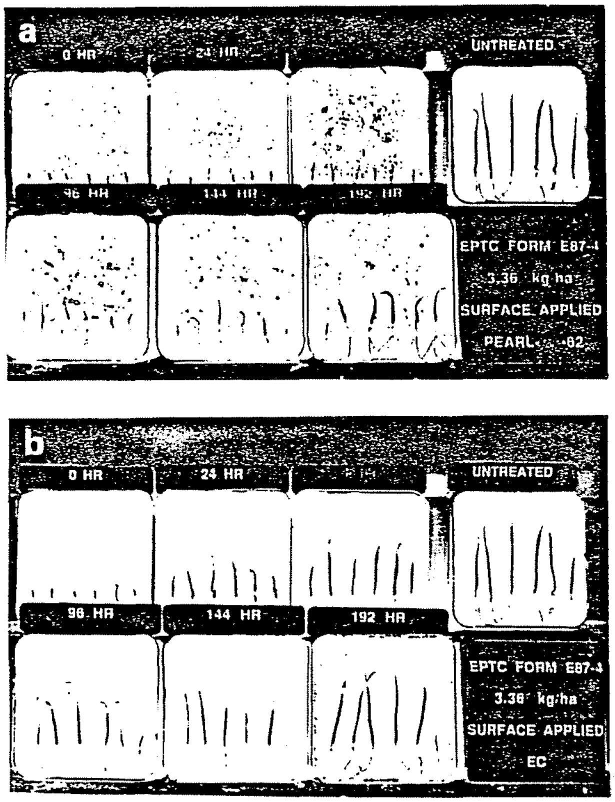

Fig. 1. Photograph of bioassay results from starch encapsulated EPTC utilizing pearl starch and the jet-cooking process. (a) Pearl starch using JC process, (b) EC formulation. Bioassays conducted 0, 24, 48, 96, 144, and 192 hours after exposure to a wet soil surface.

wet soil surface for 0 (immediately bioassayed), 24, 48, and 120 hours.

Series 2 was a comparison of the pearl B, pearl Ca–B, pearl Ca, pearl SX, pearl JC, EC and untreated check exposed on a wet soil surface for 0, 24, 48, 96, and 144 hours.

Series 3 was a comparison of the pearl Ca–B, waxy Ca–B, amylon Ca–B, waxy JC, pearl JC, amylon JC, EC and untreated check exposed on a wet soil surfaces for 0, 24, 48, 96, 144, 192, and 288 hours.

All of the bioassay data were statistically analysed using the Waller Duncan's Bayesian k-ratio t Test with a k value of 100 [12].

RESULTS

When bioassays were conducted immediately after application (0 hours), all formulations including the EC showed excellent biological activity regardless of the process used or the starting starch material (Figs. 1 to 4).

When pearl starch was used, within 24 hours all granular formulations were significantly more active than the EC formulation, and this continued through the 144 hour bioassay (Fig. 2). At 144 hours, the granular formulation prepared by the JC process had significantly more biological activity than all the other processes.

Formulations prepared with waxy, pearl and high amylose (amylon) starches using the Ca–B process showed that within 24 hours the pearl and high amylose (amylon), but not the waxy starches, were significantly more active biologically than the EC (Fig. 3). However, at 48 hours all starches produced better biologically active formulations than the EC. At 96 hours, only the waxy starch formulation was better than the EC. After 144 hours, all granular formulations were significantly more active than the EC. At 192 and 288 hours, no significant differences were noted between the untreated check and any formulation, granular or EC.

When comparisons were made among starches using the JC process, a slightly different picture appeared depending on exposure time of the granules on a wet soil surface (Fig. 4). The results at 24 hours were comparable to that of the Ca–B process in that the waxy starches were similar to the EC but, at 48 and 96 hours, the waxy starches were the same statistically as the EC. At 144 hours all granular formulations were biologically more active than the EC, but significant biological activity was extended to 192 hours with the pearl and high amylose starches. Using the JC process, all were biologically inactive by 288 hours.

Comparisons among the granular formulations indicate that the biological activity of the starches used were waxy > pearl ≥ high amylose (amylon) when the Ca–B process was used and

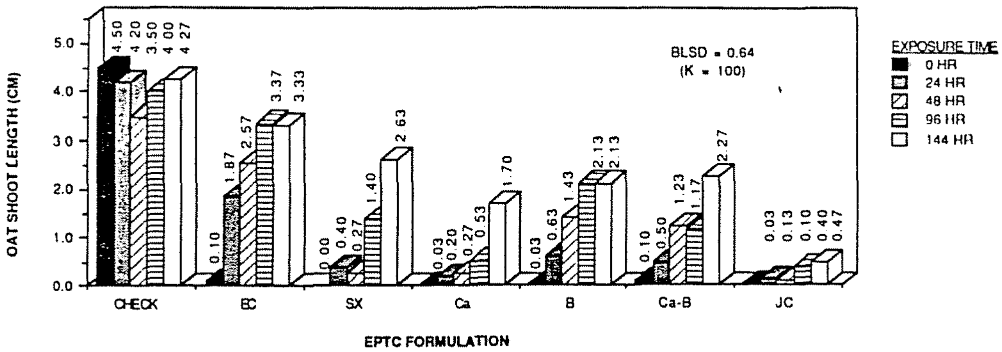

Fig. 2. Oat shoot bioassays of EPTC formulations prepared by the xanthate (SX), calcium (Ca), borate (B), calcium-borate (Ca-B), and jet-cooking process (JC) starting with pearl starch. Formulations exposed on a wet soil surface for up to 144 hours. Differences between treatments that exceed 0.64 are statistically significant.

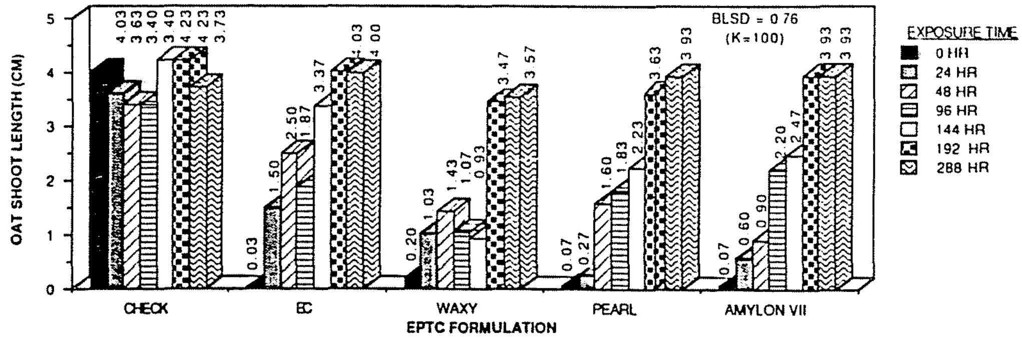

Fig. 3. Oat shoot bioassays of EPTC formulations prepared by the calcium-borate (Ca-B) process but using three different starches: waxy, pearl, and high amylose (amylon VII). Formulations exposed on a wet soil surface for up to 288 hours. Differences between treatments that exceed 0.76 are statistically significant.

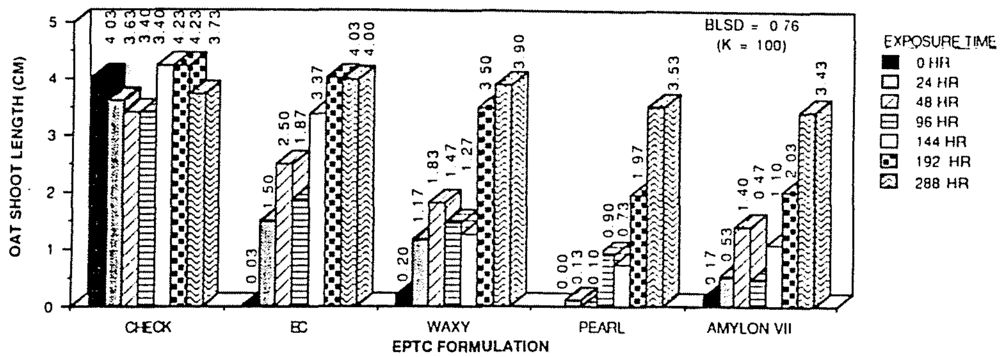

Fig. 4. Oat shoot bioassays of EPTC formulations prepared by the jet-cooking process (JC) but using three different starches: waxy, pearl, and high amylose (amylon VII). Formulations exposed on a wet soil surface for up to 288 hours. Differences between treatments that exceed 0.76 are statistically significant.

pearl ⩾ high amylose (amylon) > waxy when the JC process was used. With the Ca–B and the JC processes, the waxy starches produced granules with bimodal releases. High amylose (amylon) starch showed biomodal release only with the JC process.

DISCUSSION

Initially, all EPTC formulations were biologically active, an extremely important characteristic for herbicidal action. This may be due to the high volatility of this herbicide compared with other herbicides which have not shown immediate release [4].

With both the Ca–B and JC processes, the granular formulations prepared with the waxy starch dispersed within the first 2 and 24 hours, respectively. These data correspond with high swelling percentages in water. However, within 48 to 96 hours these same formulations increased their biological activity, indicating that, even though granules had gelatinized, some controlled release characteristic still remained. This bimodal response had not been noted before and may be related to the branched-chain character of amylopectin. All of the granular formulations showed some fungal growth since unsterilized soil was used in the bioassay. Since all starches are biodegradable and the bioassays were conducted under ideal environmental conditions (moisture and temperature) for fungal growth, the erodibility of the granular particle may have been responsible for the bimodal release noted. The pH response does not appear to be a major factor as suggested by others [8].

When formulations were prepared with pearl starch, all crosslinking technologies produced granules that were biologically more active than the EC for periods up to 96 hours. The JC process produced the most efficient formulation even up to 144 hours on a wet soil surface.

The Ca–B or the JC process used with waxy, pearl, or high amylose (amylon) starch produced different release rates based on bioassays up to 144 hours on a wet soil surface. Our biological data did not always follow the reported assumption that, as the amylose content increases, the rate of herbicide release decreases due to the ability of amylose to retrograde [10]. This may be responsible for the bimodal release noted with the waxy and high amylose (amylon) starches, depending on the process used. The waxy starch was not expected to be as effective in controlling release based on amylose content alone. In tests of waxy, pearl, and high amylose (amylon) starches using the Ca–B process, the waxy starch formulation was more biologically active than the high amylose (amylon) starch formulation.

The physical and chemical characteristics of the biologically active agent may influence which starch and process will produce the most effective controlled release formulation. In the case of EPTC, pearl or high amylose starch and the JC process would appear to be the most effective combination based on biological activity, i.e., the granules produced retain their integrity longer, thus producing longer controlled release.

CONCLUSIONS

The biological activity of starch-encapsulated granules containing EPTC and the rate of their release, a measure of the integrity of the granule, depends on the nature of the starch used and the crosslinking process. Retaining the activity of the highly volatile herbicide EPTC on a wet soil surface for 6 to 8 days has been accomplished by encapsulation utilizing several crosslinking techniques (both chemical and non-chemical) and starches with different ratios of amylopectin and amylose. It would appear that in the case of the herbicide EPTC, encapsulation on a pearl or high amylose starch utilizing the JC process produces the best controlled release formulation even under the most adverse conditions.

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